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(54) **Pickling of stainless steels while continuously reoxidizing catalytically the pickling solution**

Beizen von rostfreien Stählen mit kontinuierliche katalytische Oxidation der Beizlösung

Décapage d'aciers inoxydables en réoxident catalytiquement continuellement la solution de décapage

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<b>US-A- 2 720 472</b>	<b>US-A- 3 542 508</b>
<b>US-A- 3 682 592</b>	<b>US-A- 3 928 529</b>
<b>US-A- 4 166 098</b>	<b>US-A- 4 248 851</b>

- **PATENT ABSTRACTS OF JAPAN** vol. 013, no. 431 (C-640), 26 September 1989 & JP-A-01 165783 (KAWASAKI STEEL CORP), 29 June 1989,
- **PATENT ABSTRACTS OF JAPAN** vol. 006, no. 231 (C-135), 17 November 1982 & JP-A-57 134564 (MITSUBISHI KASEI KOGYO KK; OTHERS: 01), 19 August 1982,

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## Description

[0001] Pickling of stainless steel (austenitic, martensitic and ferritic) and of other special alloys is usually performed with strongly acid mixtures in presence of an oxidizing agent.

[0002] The latter, besides performing a direct action in the pickling process itself, attend to the dissolution of an eventually present dechromized surface layer caused by a heat treatment, as well as to the passivation of the material, thus conferring to it stainless characteristics.

[0003] The oxidizing agent traditionally used for this type procedure is nitric acid and a typical bath utilized for the pickling of stainless steels usually employs mixtures of nitric acid and hydrofluoric acid, to which hydrochloric acid and other pickling coadjuvants such as inhibitors, wetting agents, foam promoters, and the like, may be added.

[0004] Traditionally, nitric acid has been widely used because of its low cost if compared to other more expensive oxidizing agents.

[0005] With the ever increasing environmental and safety consciousness, the use of nitric acid has recently been questioned.

[0006] The problems associated with the use of nitric acid can be summarized in three fundamental issues:

### a) Water pollution

[0007] Nitrates and nitrites constitute a source of nourishment for sea weeds and therefore contribute to eutrophization phenomena.

[0008] Nitrites form nitrosamine which are in turn assimilated by fish and may constitute a cause factor in the insurgence of cancer if ingested.

[0009] At present, an economically viable technique that can be adopted by the metal industry in general to eliminate nitrites and nitrates from effluents is not at hand. This has created major difficulties in complying with effluent control normative as enacted by governments, such as in Italy.

### b) Air pollution

[0010] The reduction reaction on nitric acid envisages the formation of nitrogen oxides represented by the general formula NO<sub>x</sub>, which are characterized by their reddish color.

[0011] These fumes, besides being toxic for may living organisms, contribute to the ill known phenomena of acid rain and as a consequence their emission in the atmosphere is regulated in almost all developed countries.

### c) Toxicity for the operator

[0012] The Chemistry Encyclopaedia (UTET) reads:

"Nitric acid, its fumes and other nitrogen oxides have a high level of toxicity that in serious cases may even lead to death".

[0013] Therefore, remarkable efforts have been undertaken by the industry to eliminate or reduce the problems caused by the use of this acid.

[0014] Many studies and patents have been realized in this field.

[0015] A first approach was that of eliminating the emission of nitrogen oxides in the atmosphere. Samples of these generally known proposals are:

- reoxidation to nitrates in special abatement columns by the use of hydrogen peroxide or manganate/permanganate mixtures;
- reduction to nitrogen in special abatement columns by the use of urea;
- catalytic combustion at high temperature;
- bath reoxidation by injecting hydrogen peroxide in function of the monitored redox potential (as described in the Swedish Patent No. SE 8305648).

[0016] To the techniques developed for reducing the emissions of nitrogen oxides in the atmosphere have been added techniques for limiting the release of nitrates and nitrites in effluent liquors. Among these techniques the following have met an industrial use:

- the regeneration of baths by electrodialysis, ion exchange and roasting;
- the recovering of rinse water by inverse osmosis or evaporation;
- reduction of nitrites via electrolysis or by the use of sulfamic acid.

[0017] However, in all the above cases, working conditions are generally improved but the problem is not completely eliminated.

[0018] On the other hand, important steps forward have been made in the last decade toward eliminating altogether the use of nitric acid.

[0019] All the techniques developed for this purpose practically make use of hydrogen peroxide as the oxidizing agent.

[0020] On a case to case basis, hydrogen peroxide acts as a direct oxidizing agent or as an oxidizer vehicle when the oxidizing action is actually carried out by trivalent iron, commonly present in the pickling solution.

[0021] Various complex reactions of oxidation take place in the pickling bath even if most frequently the predominant role is attributable to trivalent iron (Fe<sup>+++</sup> or Fe<sup>3+</sup>) which exerts its oxidizing action by reducing itself to bivalent iron (Fe<sup>++</sup> or Fe<sup>2+</sup>) so that the function of add-

ing hydrogen peroxide to the pickling bath would be, in this case, that of reoxidizing the bivalent iron to trivalent iron.

**[0022]** In reality, it is generally accepted the fact that during the pickling process both hydrogen peroxide and trivalent iron play a role.

**[0023]** Among any patents issued in this field, the following may be cited.

- The Japanese Patent No. 243289/85 of Kobe Steel describes the use of a pickling mixture of hydrofluoric acid, hydrogen peroxide and, eventually hydrochloric acid and/or sulphuric acid.
- The Patent No. DE 2,827,697 describes pickling conducted in a solution of sulphuric acid, hydrofluoric acid and ferric sulphate into which hydrogen peroxide is added to maintain the correct redox potential.

**[0024]** The high operation cost due to the large consumption of hydrogen peroxide in these processes has promoted the search of techniques aimed to reduce such a consumption.

**[0025]** A first attempt was made by the French company Ugine who, among the many patents obtained, own the European Patent No. EP 0 236 354, wherein the blowing of air through the pickling bath is disclosed as a coadjuvant of hydrogen peroxide. However, the rate of reaction of the oxygen at the typically low pH of the pickling bath is so low that it does not achieve any considerable saving, least of all an elimination of hydrogen peroxide addition.

**[0026]** For these reasons, special stabilizing agents have been developed and patented in order to stabilize the hydrogen peroxide even in presence of a high concentration of iron in the solution.

**[0027]** The Italian Patent No. 1,246,252 of the Italian company CONDORIL CHEMICAL, discloses the use of aliphatic tertiary alcohols as specific stabilizing agents for pickling solutions of stainless steel that utilize hydrogen peroxide and sulphuric acid in total substitution of nitric acid.

**[0028]** However, even in this process, the consumption of hydrogen peroxide and of stabilizers implies still relatively high operation costs, especially the treating large volumes of stainless steel.

**[0029]** The Japanese patent application JP-A-01165783 discloses a process and apparatus for regenerating an HF and ferric ions containing stainless steel pickling solution by oxidizing the ferrous ions with air.

**[0030]** US-A-3,928,529 discloses a regeneration process for spent pickle liquor comprising the oxidizing of an aqueous solution of ferrous chloride and hydrochloric acid in presence of activated carbon to form aqueous ferric chloride which is then hydrolyzed to about 232°C to obtain vaporized hydrochloric acid and iron oxide.

**[0031]** US-A-4,166,098 describes a process for recovering sulfuric acid from an acid waste liquor containing Fe ions employing organic solvents for extracting the mineral acid.

**[0032]** US-A-3,542,508 discloses a continuous method of oxidizing ferrous compounds to ferric compounds by passing a solution and oxygen through a bed of catalytic noble metal supported on an inert material as a route to recovering iron contained in sulfuric or hydrochloric acid solutions.

**[0033]** In the light of these known techniques and of their associated limitations and costs, a pickling process has now been found which is outstandingly more efficient and more economical to run if compared to the known processes.

**[0034]** This innovative pickling process eliminates completely any addition of hydrogen peroxide and also of the stabilizing agents that would eventually be required, achieving a surprising reduction of pickling costs while ensuring a most effective control of the emission of pollutants.

**[0035]** Despite of the fact that according to a particularly preferred embodiment the process of the present invention there is absence of nitric acid in the pickling solution, the invention remains effective even in presence of nitric acid in the pickling solution, which is still the case in the majority of existing plants. Indeed the process of the invention permits reoxidization of the reduction compounds of this acid, that is it is capable of reoxidizing NOx back to nitric acid.

**[0036]** The invention provides a method for pickling steel or ferrous alloys as defined in claim 1.

**[0037]** Basically, as defined in claim 1, an effective reoxidizing of the pickling liquor is performed by passing the solution and a gas mixture containing oxygen or pure oxygen gas through a fluidized bed containing a noble metal catalyst supported on a material that is chemically inert to the pickling solution.

**[0038]** The invention also provides a pickling plant for steel or ferrous alloys as defined in claim 8.

**[0039]** The catalytic bed may be composed of granular material and/or bodies of different shapes.

**[0040]** The bed may be for example fluidized by injecting from beneath, through a plurality of nozzles the pickling liquor and/or a gas mixture containing oxygen or pure oxygen, which may be premixed together during the injection phase using special ejectors.

**[0041]** Basically it is important to ensure the largest number of points of contact among the catalyst, the reduced ions to be reoxidized and oxygen.

**[0042]** In this respect, it has now been found that the reoxidation kinetics remains high even in case the catalytic bed is completely flooded by the liquor and the gas mixture containing oxygen or the pure oxygen is bubbled through the solution that completely floods the catalytic bed.

**[0043]** A noncatalytic static bed may be present to enhance uniformity of distribution of the stream of the so-

lution and solution of oxygen in liquid before the latter comes into contact with the fluidized catalytic bed.

[0044] It has been found that in this way it is possible to completely eliminate the consumption of hydrogen peroxide and consequently the costs associated with this consumption as well as with that of eventual hydrogen peroxide stabilizers, as normally used for reducing the consumption of hydrogen peroxide.

[0045] Moreover, according to the method of the invention, there is no need to blow air through the pickling bath, being this a practice that aggravates the problems associated with the emission of fumes.

[0046] The most surprising aspect of the process of the invention is the amount of the reduction of the costs of the pickling processing if compared with those relative to a process without nitric acid and based on hydrogen peroxide addition for reoxidizing iron and nitrogen suboxides and on the addition of stabilizers to control the hydrogen peroxide consumption.

[0047] Based on the current market price of hydrogen peroxide and of the stabilizers most commonly used, a comparison of pickling costs with the novel process of the invention, taking into consideration the cost of compressing air or the cost of compressed oxygen, reveals a saving in favor of the process of the invention of 90% to 98% of the cost of the known processes.

[0048] Thermodynamically, oxidation of bivalent iron to trivalent iron or of NOx into nitric acid using oxygen would appear possible, nevertheless all prior attempts to use air as an oxidizing agent by bubbling it through the pickling bath have yielded scarce or null results.

[0049] According to state of the art techniques, addition of hydrogen peroxide in the pickling bath as reoxidizing agent of bivalent iron to trivalent iron, or of NOx to nitric acid is often accompanied by the blowing of air through the bath, merely as an efficient way of stirring the bath.

[0050] Indeed, the reoxidation reaction of bivalent iron to trivalent iron, or of NOx to nitric acid, although being thermodynamically favored, is kinetically impeded from progressing in acid solutions under normal temperature and pressure conditions. Attempts made with pure oxygen in place of air or by increasing the partial pressure of the oxygen and/or the temperature or by nebulizing the pickling liquor in order to improve the exchange conditions have yielded disappointingly scarce results.

[0051] By contrast, it has now been found that by contacting the pickling solution and the oxygen, on a fluidized catalytic bed, containing a noble metal such as platinum supported onto the surface of an inert material that is not chemically attacked by the pickling solution, such as for example carbon, an extremely efficient reoxidation of bivalent iron to trivalent iron and/or of NOx to nitric acid is achieved with extremely satisfactory contact times and yields of conversion.

[0052] Noble metals like Pt, Pd, Ru, Rh, Au, and their alloys are among the catalysts that have shown to be effective in ensuring a satisfactory kinetics of the reoxi-

dation reaction of bivalent iron and/or of NOx contained in the solution coming from the pickling bath to trivalent iron and nitric acid, respectively. The noble metal is supported on an inert support material that is not chemically attacked by the pickling solution. Carbonaceous materials such as carbon, carbon black, barium sulphate and plastic materials such as polypropylene and ABS are examples of suitable supports.

[0053] The best results were obtained with platinum supported on granular coal or on a high specific surface carbon dust.

[0054] The yield in function of oxygen consumption is higher when using pure oxygen if compared to the yield obtained using air compressed at a pressure five times higher than that of pure oxygen (so as to bring the latter to a comparable partial pressure) However, this aspect does not represent a critical choice in terms of operating costs.

[0055] Depending on the type of embodiment the liquid may elute in countercurrent or in equicurrent mode to the gas mixture containing oxygen or to the pure oxygen that may even be bubbled through a flooded fluidized catalytic bed.

[0056] Reoxidation of bivalent iron and/or of NOx takes place primarily in the catalyzed portion of the bed.

[0057] Figure 1 shows a possible scheme of the reoxidation section of a pickling system, comprising a reoxidising reactor as defined in claim 8. Figures 2 and 3 show suitable configurations of each one of the two reoxidation columns employed in the system of Fig. 1.

[0058] In a pilot plant realized according to the scheme of Fig. 1, using two reoxidation columns in cascade having a configuration as that illustrated in Figures 2 and 3, a number of tests were run with the purpose of demonstrating the effectiveness of the invention when applied to a commercial pickling process already operating according to the teachings contained in the Italian Patent No. 1,246,252. of CONDOROIL CHEMICAL.

[0059] By referring to Fig. 2, each reactor was constituted by a cylindrical vessel 1 closed at its two ends made of an acid resistant plastic material such as polypropylene. It could also be made of ebonized steel or of any other material chemically resistant to the pickling liquor.

[0060] According to this embodiment, the column had a first portion 2 of a static bed constituted by polypropylene saddles, resting upon a grid of polypropylene 3 that separated the upper part 4a, having a larger diameter, from the lower part 4b, having a reduced diameter, of a packaging containment pipe of polypropylene.

[0061] A second grid 5 of polypropylene defined the space occupied by a catalyzed bed 6 of platinum supported onto coal granules (catalyzer ESCAT 28D produced by the U.S. company ENGELHARD). The pickling liquor was introduced through the top nozzle 9 and distributed above the bed 2 by means of a plurality of spreader nozzles 7.

[0062] The catalytic bed 6 of platinum supported on

coal granules is fluidized by injecting compressed air through a plurality of nozzles 8.

[0063] The liquor coming from the pickling bath percolated through the bed 2 and eluted in countercurrent to the compressed air bubbled through the fluidized catalyzed bed 6 and flowed out of the reactor through the nozzle 10.

[0064] The excess air was continuously vented through the outlet 11.

[0065] The process of the invention has been tested also in laboratory scale for different pickling bath conditions and all the results confirm its exceptional effectiveness in the tested cases of baths containing ferric ions and/or nitric acid and comprising :

- from 1 to 80 g/l of hydrofluoric acid and/or of salts thereof;
- from 0 to 200 g/l of nitric acid and/or of salts thereof;
- from 0 to 200 g/l of sulphuric acid and/or of salts thereof;
- from 0 to 150 g/l of other inorganic acids belonging to the group composed of fluoroboric acid, phosphoric acid and of organic acids such as citric acid and/or salts thereof;
- from 0 to 50 g/l of  $\text{Fe}^{2+}$ ;
- from 0 to 150 g/l of  $\text{Fe}^{3+}$ .

[0066] The effectiveness of the invention has been tested also in the case of a most traditional pickling process employing a mixture of nitric acid and hydrofluoric acid with and without addition of sulphuric acid.

[0067] Also these tests were carried out in laboratory and have not yet repeated in a pilot plant.

[0068] The parameter that was observed was the concentration of nitrogen oxides ( $\text{NO}_x$ ) in the fumes released by the pickling solution when the liquor was and was not circulated through a reoxidation reactor fed with oxygen and equipped with the same catalyzer used in the pilot plant.

[0069] These tests demonstrated a marked reduction of the concentration of nitrogen oxides ( $\text{NO}_x$ ) in the fumes when the solution was continuously reoxidized and recycled to the pickling bath.

[0070] Fig. 3 shows another embodiment of a reoxidation reactor for the pickling solution.

[0071] According to this embodiment, the reoxidation column contains a fluidized catalytic bed 6 confined between the upper grid 3 and the bottom grid 5 that is maintained in a fluidized state by the solution premixed with oxygen which is injected through a plurality of nozzles 8. In this case through the outlet 10+11 placed at the top of the column both the reoxidized solution and the excess gas and/or oxygen are released.

[0072] Mechanical stirrers may also be employed for fluidizing the catalytic bed or to promote contact among the reacting phases.

## Claims

1. A process of pickling stainless steel of ferrous alloys which comprises contacting the steel or ferrous alloy to be pickled with an aqueous acid solution containing at least a reducible oxidizing agent belonging to the group composed of ferric ions and nitric acid, treating a portion of the pickling solution in a separate reactor to reoxidize the reduced oxidizing agent by contacting the solution with oxygen and recycling the solution treated into the pickling bath, characterized in that the oxidizing step is performed by passing the solution and a gas mixture containing oxygen or pure oxygen gas through a fluidized bed containing a noble metal catalyst supported on a material that is chemically inert to the pickling solution.
2. The process according to claim 1, characterized in that the bed is flooded with pickling solution and is fluidized by means of compressed air injected at the bottom of the bed.
3. The process according to claim 1, characterized in that the bed is fluidized by injecting the pickling solution premixed with a gas mixture containing oxygen or pure oxygen gas at the bottom of the bed.
4. The process according to claim 1, characterized in that said aqueous acid solution containing an oxidizing agent reducible during the pickling and that is reoxidized comprises:
  - from 1 to 80 g/l. of hydrofluoric acid and/or of salts thereof;
  - from 0 to 200 g/l. of sulphuric acid and/or of salts thereof;
  - from 0 to 200 g/l. of nitric acid and/or of salts thereof;
  - from 0 to 150 g/l. of other inorganic acids belonging to the group composed of fluoroboric acid and phosphoric acid and organic acids and/or of salts thereof;
  - from 0 to 50 g/l. of  $\text{Fe}^{2+}$ ; and
  - up to 150 g/l. of  $\text{Fe}^{3+}$ .
5. The process according to claim 1 characterized in that said oxidizing agent is a soluble ferric compound, the trivalent iron ion in the solution constituting an oxidizing agent being reduced to bivalent ions of iron that are reoxidized to trivalent ions of iron.
6. The process according to claim 1, characterized in that said oxidizing agent is nitric acid the pentavalent nitrogen ion constituting an oxidizing agent being reduced to subvalent nitrogen ion ( $\text{NO}_x$ ) that is reoxidized to a pentavalent nitrogen ion.

7. The process according to claim 1, characterized in that said noble metal is selected from the group composed of palladium, platinum, gold and alloys thereof, and said inert material is selected from the group composed of carbon, barium sulphate, polypropylene and ABS. 5
8. A pickling plant for steel or ferrous alloys comprising a pickling bath of an aqueous acid solution containing at least a soluble oxidizing compound belonging to the group composed of ferric ions and nitric acid reducible in the pickling solution, a flow path of said solution including filtering means, means for reoxidizing and recycling the reoxidized pickling liquor in said bath (re: page 5, lines 13-16), characterized in that said circuit comprises at least a reoxidizing reactor (1) containing a fluidized catalytic bed (6) of a noble metal catalyst supported on particles of a material chemically inert in the pickling solution, confined between a top (3) and a bottom (5) grid, inlet and outlet means for passing said pickling liquor (9, 10) through said catalytic bed (6) and for injecting a fluidizing stream of at least a gas mixture containing oxygen or pure oxygen gas (12, 8) at the bottom of said bed and a gas outlet (11) at the top of the reactor. 10 15 20 25
9. The pickling plant according to claim 8, characterized in that said supported catalyst is a carbon supported platinum catalyst. 30
10. The pickling plant according to claim 8, characterized in that said pickling solution is premixed with said gas mixture containing oxygen or pure oxygen gas and injected at the bottom of said bed. 35

#### Patentansprüche

1. Verfahren zum Beizen von rostfreiem Stahl eisenhaltiger Legierungen, das das Kontaktieren des Stahls oder der eisenhaltigen Legierung, die mit einer wässrigen Säurelösung gebeizt werden soll, die wenigstens ein reduzierbares Oxidationsmittel enthält, das zu der Gruppe gehört, die aus Eisenionen und Salpetersäure besteht, das Behandeln eines Teils der Beizlösung in einem separaten Reaktor, um das reduzierte Oxidationsmittel durch Kontaktieren der Lösung mit Sauerstoff zurückzuoxidierten, und das Wiederverwenden der behandelten Lösung in dem Beizbad umfaßt, dadurch gekennzeichnet, daß der Oxidationsschritt mittels Leiten der Lösung und eines Gasgemisches, das Sauerstoff oder reines Sauerstoffgas enthält, durch ein Fließbett, das einen Edelmetallkatalysator enthält, der von einem Material getragen wird, das chemisch inert zu der Beizlösung ist, durchgeführt wird. 40 45 50 55

2. Verfahren gemäß Anspruch 1, dadurch gekennzeichnet, daß das Bett mit Beizlösung überflutet und mittels komprimierter Luft, die am Boden des Bettes eingespritzt wird, verwirbelt wird.
3. Verfahren gemäß Anspruch 1, dadurch gekennzeichnet, daß das Bett durch Einspritzen der Beizlösung, die zuvor mit einem Gasgemisch, das Sauerstoff oder reines Sauerstoffgas enthält, gemischt wurde, am Boden des Bettes verwirbelt wird.
4. Verfahren gemäß Anspruch 1, dadurch gekennzeichnet, daß besagte wässrige Säurelösung, die ein Oxidationsmittel enthält, das während des Beizens reduzierbar ist, und das zurückoxidiert wird,
  - 1 bis 80 g/l Fluorwasserstoffsäure und/oder Salze davon;
  - 0 bis 200 g/l Schwefelsäure und/oder Salze davon;
  - 0 bis 200 g/l Salpetersäure und/oder Salze davon;
  - 0 bis 150 g/l andere anorganische Säuren, die zur der Gruppe gehören, die aus Fluorbor-säure und Phosphorsäure besteht, und organische Säuren und/oder Salze davon;
  - 0 bis 50 g/l  $\text{Fe}^{2+}$  und
  - bis zu 150 g/l  $\text{Fe}^{3+}$  umfaßt.
5. Verfahren gemäß Anspruch 1, dadurch gekennzeichnet, daß besagtes Oxidationsmittel eine lösliche Eisenverbindung ist, wobei das dreiwertige Eisenion in der Lösung ein Oxidationsmittel bildet, das zu zweiwertigen Eisenionen reduziert wird, die zu dreiwertigen Eisenionen zurückoxidiert werden. 30 35
6. Verfahren gemäß Anspruch 1, dadurch gekennzeichnet, daß besagtes Oxidationsmittel Salpetersäure ist, wobei das fünfwertige Stickstoffion ein Oxidationsmittel bildet, das zum unterwertigen Stickstoffion ( $\text{NO}_x$ ) reduziert wird, das zu einem fünfwertigen Stickstoffion zurückoxidiert wird.
7. Verfahren gemäß Anspruch 1, dadurch gekennzeichnet, daß das Edelmetall aus der Gruppe ausgewählt wird, die aus Palladium, Platin, Gold und Legierungen davon besteht, und besagtes inertes Material aus der Gruppe ausgewählt wird, die aus Kohlenstoff, Bariumsulfat, Polypropylen und ABS besteht.
8. Beizwerk für Stahl oder Eisenlegierungen, das ein Beizbad aus einer wässrigen Säurelösung, die wenigstens eine lösliche oxidierende Verbindung enthält, die zu der Gruppe gehört, die aus Eisenionen und Salpetersäure besteht, die in der Beizlösung reduzierbar sind, und einen Fließweg besagter Lösung umfaßt, einschließlich Filtermittel, Mittel

für die Rückoxidation und Wiederverwendung der rückoxidierten Beizlösung in gesagtem Bad (siehe Seite 5, Zeilen 13 bis 16), dadurch gekennzeichnet, daß besagter Kreislauf wenigstens einen Rückoxidiationsreaktor (1), der ein verwirbeltes katalytisches Bett (6) eines Edelmetallkatalysators enthält, der von Partikeln eines Materials getragen wird, die chemisch inert in der Beizlösung sind, und das sich zwischen einem Obergitter (3) und einem Bodengitter (5) erstreckt, Einlaß- und Auslaßmittel zum Leiten besagter Beizlösung (9, 10) durch besagtes katalytisches Bett (6) und zum Einspritzen eines Wirbelstroms aus wenigstens einem Gasgemisch, das Sauerstoff oder reines Sauerstoffgas (12, 8) enthält, am Boden des besagten Bettes und einen Gasauslaß (11) an der Oberseite des Reaktors umfaßt.

9. Beizwerk gemäß Anspruch 8, dadurch gekennzeichnet, daß besagter Trägerkatalysator ein von Kohlenstoff getragener Platinkatalysator ist.
10. Beizwerk gemäß Anspruch 8, dadurch gekennzeichnet, daß besagte Beizlösung zuvor mit besagtem Gasgemisch, das Sauerstoff oder reines Sauerstoffgas enthält, gemischt und am Boden des besagten Bettes eingespritzt wird.

#### Revendications

1. Procédé de décapage d'acier inoxydable ou d'alliage ferreux qui comprend les étapes consistant à mettre en contact l'acier ou l'alliage ferreux à décapager avec une solution acide aqueuse contenant au moins un agent oxydant réductible appartenant au groupe comprenant les ions ferriques et l'acide nitrique, à traiter une partie de la solution de décapage dans un réacteur séparé pour réoxyder l'agent d'oxydation réduit en mettant la solution en contact avec de l'oxygène, et à recycler la solution traitée dans le bain de décapage, caractérisé en ce que l'étape d'oxydation est réalisée en faisant passer la solution et un mélange gazeux contenant de l'oxygène ou de l'oxygène pur dans un lit fluidisé contenant un catalyseur à métal noble porté sur un matériau chimiquement inerte pour la solution de décapage.
2. Procédé selon la revendication 1, caractérisé en ce que le lit est inondé par la solution de décapage et est fluidisé au moyen d'air comprimé injecté au fond du lit.
3. Procédé selon la revendication 1, caractérisé en ce que le lit est fluidisé en injectant la solution de décapage prémélangée avec un mélange gazeux contenant de l'oxygène ou de l'oxygène pur au fond

du lit.

4. Procédé selon la revendication 1, caractérisé en ce que la solution acide aqueuse contenant un agent oxydant réductible pendant le décapage et qui est réoxydée comprend :
  - de 1 à 80 g/l d'acide fluorhydrique et/ou de ses sels ;
  - de 0 à 200 g/l d'acide sulfurique et/ou de ses sels ;
  - de 0 à 200 g/l d'acide nitrique et/ou de ses sels ;
  - de 0 à 150 g/l d'autres acides minéraux appartenant au groupe comprenant l'acide fluoroborique, l'acide phosphorique et des acides organiques et/ou leurs sels ;
  - de 0 à 50 g/l de  $\text{Fe}^{2+}$  ; et
  - de 0 à 150 g/l de  $\text{Fe}^{3+}$ .
5. Procédé selon la revendication 1, caractérisé en ce que l'agent oxydant est un composé ferrique soluble, les ions fer trivalents dans la solution constituant un agent oxydant étant réduits en ions fer bivalents qui sont réoxydés en ions fer trivalents.
6. Procédé selon la revendication 1, caractérisé en ce que l'agent oxydant est de l'acide nitrique, l'ion azote pentavalent constituant un agent oxydant étant réduit en ion azote sous valent  $\text{NO}_x$  qui est réoxydé en un ion hydrogène pentavalent.
7. Procédé selon la revendication 1, caractérisé en ce que le métal noble est choisi dans le groupe comprenant le palladium, le platine, l'or et leurs alliages, et le matériau inerte est choisi dans le groupe comprenant le carbone, le sulfate de baryum, le polypropylène et l'ABS.
8. Installation de décapage pour acier et alliages ferreux comprenant un bain de décapage d'une solution acide aqueuse contenant au moins un composé oxydant soluble appartenant au groupe comprenant les ions ferriques et l'acide nitrique réductibles dans la solution de décapage, un trajet de circulation de la solution comprenant un moyen de filtrage, un moyen de réoxydation et de recyclage du liquide de décapage réoxydé dans le bain (voir page 6 lignes 11-15), caractérisé en ce que le circuit comprend au moins un réacteur de réoxydation (1) contenant un lit catalytique fluidisé (6) d'un catalyseur à métal noble porté sur des particules d'un matériau chimiquement inerte dans la solution de décapage, confiné entre une grille supérieure (3) et une grille inférieure (5), des moyens d'entrée et de sortie pour faire passer le liquide de décapage (9, 10) dans le lit catalytique (6) et pour injecter un flux fluidisant d'au moins un mélange gazeux contenant de l'oxygène ou de l'oxygène pur (12, 8) au fond du lit et

une sortie de gaz (11) en haut du réacteur.

9. Installation de décapage selon la revendication 8, caractérisée en ce que le catalyseur porté est du platine catalyseur porté par du carbone. 5
10. Installation de décapage selon la revendication 8, caractérisée en ce que la solution de décapage est prémélangée avec un mélange gazeux contenant de l'oxygène ou avec de l'oxygène pur, et injectée au fond du lit. 10

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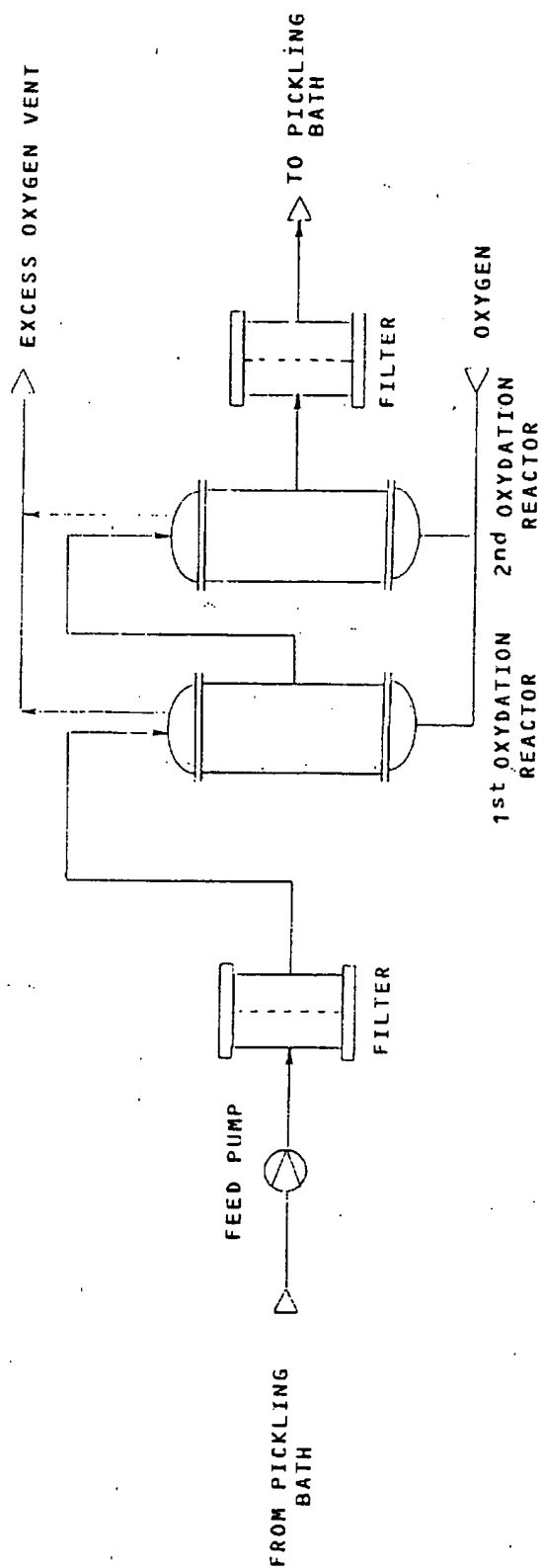


FIG. 1

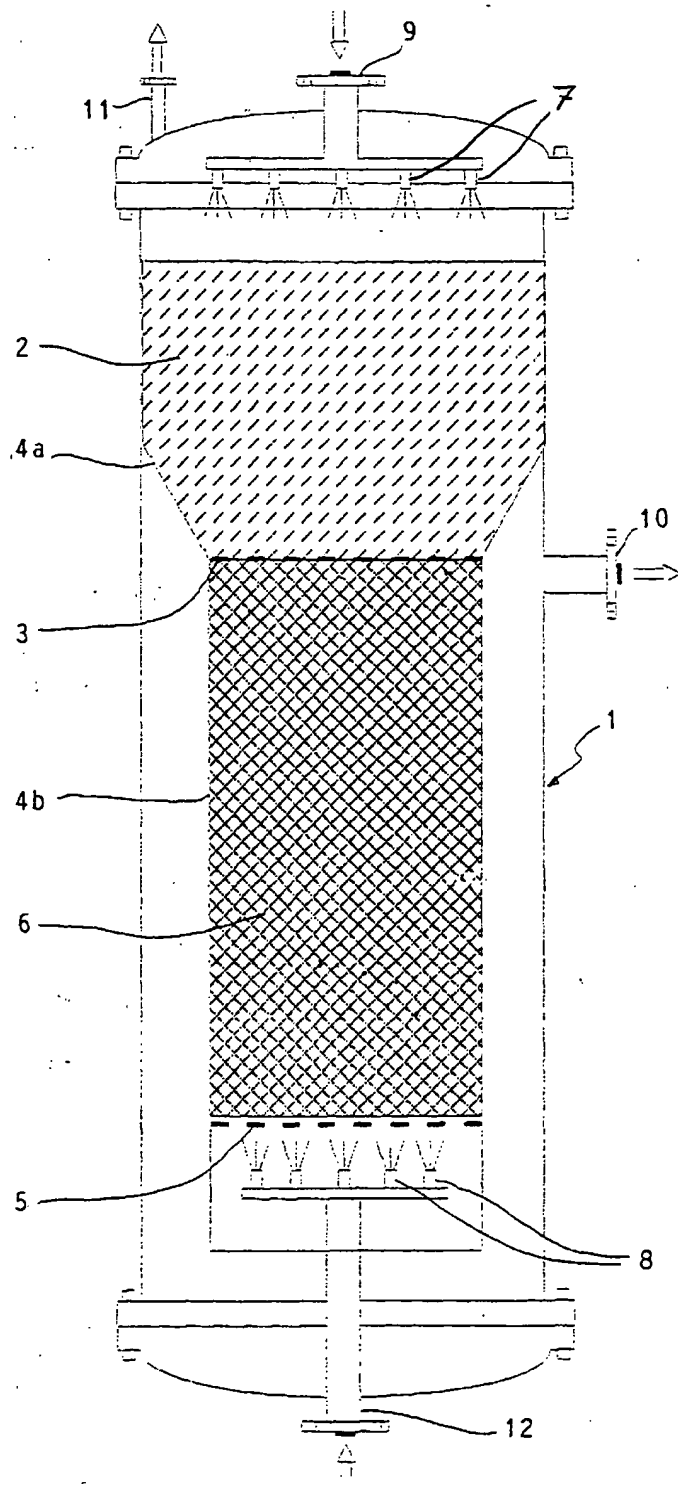


FIG. 2

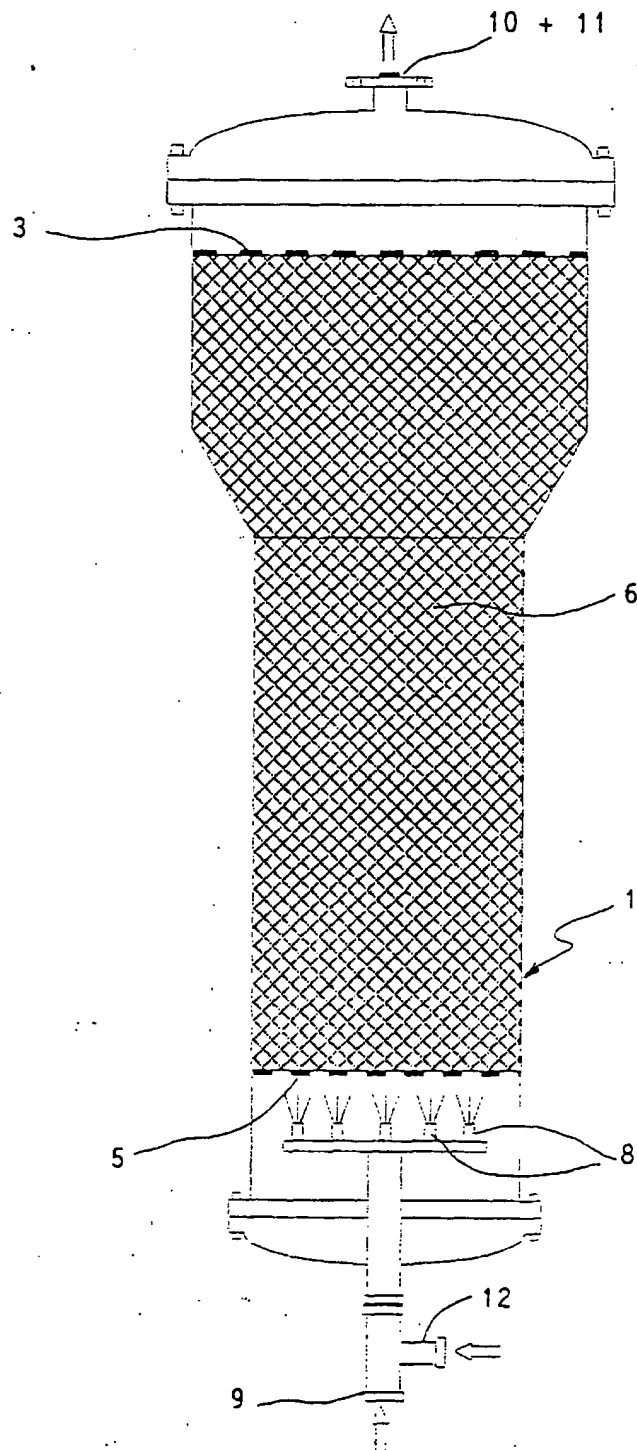


FIG. 3